GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: 2/6/80

Project Title: Porphyrin Ions in Metabolism: Physical Properties

Project No: G-33-M02

Project Director: Dr. R. H. Felton

Sponsor: DHEW/PHS/NIH - National Institute of Arthritis, Metabolism & Digestive Diseases

Agreement Period: From 1/1/80 Until 12/31/80 (11 year)

Type Agreement: Grant No. 5 R01 AM14344-11

Amount: $90,857 New PHS Funds (G-33-M02)
5,505 GIT Contribution (G-33-354)
$96,362 Total

Reports Required: Annual Progress Reports w/Continuation Applications, Terminal Progress Report upon Grant Expiration

Sponsor Contact Person (s):

Technical Matters

Robert Katz, PH.D.
Chief, Metabolic Diseases Research
Program Director
Extramural Programs
National Institute of Arthritis,
Metabolism, & Digestive Diseases
Bethesda, MD 20014

Contractual Matters
(thru OCA)

Linden F. Neff
Grants Management Officer, EP
National Institute of Arthritis,
Metabolism, & Digestive Diseases
Bethesda, MD 20014

Defense Priority Rating: none

Assigned to: Chemistry (School/~~Laboratory~~)

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GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION SHEET

Date September 1, 1983

Project Title: "Porphyrin Ions and Radicals in Metabolism: Physical Properties"

Project No: G-33-M02

Project Director: Dr. R. H. Felton

Sponsor: National Institute of Arthritis, Metabolism and Disgestive Diseases

Effective Termination Date: 12/31/80

Clearance of Accounting Charges: 3/31/81

Grant/Contract Closeout Actions Remaining:

- ☐ ~~Final Invoice and Closing Documents~~ ROE prepared 4/21/81
- ☐ Final Fiscal Report
- ☒ Final Report of Inventions
- ☐ Govt. Property Inventory & Related Certificate
- ☐ Classified Material Certificate
- ☐ Other _____

Assigned to: Chemistry (School/~~Laboratory~~)

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FORM OCA 10/78

Final Report G-33-1102

SECTION IV

APPLICANT: REPEAT GRANT NUMBER SHOWN ON PAGE 1 →	GRANT NUMBER
SECTION IV—SUMMARY PROGRESS REPORT	AM 14344
PRINCIPAL INVESTIGATOR OR PROGRAM DIRECTOR (Last, First, Initial)	PERIOD COVERED BY THIS REPORT
Felton, Ronald H.	FROM: 01/01/80 — THROUGH: 10/10/80
NAME OF ORGANIZATION: Georgia Institute of Technoloby	

TITLE (Repeat title shown in Item 1 on first page)

Prophyrin Ions in Metabolism: Physical Properties

1. List publications: (a) published and not previously reported; (b) in press. Provide five reprints if not previously submitted.
2. List all additions and deletions in professional personnel and any changes in effort.
3. Progress Report. (See Instructions)

1b. Semi-empirical LCAO-Xα Theory for Transition Metal Complexes I. Theory, Chemical Physics 000 (1981).

Semi-empirical LCAO-Xα Theory for Transition Metal Complexes II. Application to Ionization Potentials, Chemical Physics 000 (1981).

2. Deletion of Personnel
T. H. Mabry - Technical Asst/part-time.

3. see attached pages.

IV.3 Progress Report 01/01/80 - 10/10/80

The overall objectives are

(1) Development and application of the LCAO-Xα theory to transition metal complex electronic structure.

(2) Study of the mechanism of resonance Raman (RR) enhancement of axial ligand modes of metalloporphyrins via charge-transfer transitions.

(3) Synthesis of ferric porphyrins exhibiting properties consonant with those of Compounds I and II of horse radish peroxidase.

(4) Study of electron-transfer mechanism in metalloporphyrins.

Goals set for the period 01/01/81 - 12/31/81 are

(1) Application of the LCAO-Xα theory to metalloporphyrins.

(2) Examination of the 874 cm^{-1} $\nu(Os=O)$ and phenolate RR excitation profiles.

(3) Synthesis of a hindered ferric porphyrin which cannot undergo dimerization but will bind OH^-.

(4) Assembly of components for a nanosecond spectrometer and examination of covalently linked porphyrins.

Results of the past year and future research goals are discussed together.

The semi-empirical LCAO-Xα theory is implemented for transition metals. Using photoelectron data of seventeen carbonyl and oxyhalogen complexes, we reproduced well the experimental ionization potentials; indeed, far better than extended Huckel models. An important finding is that 4s and 4p levels should be excluded in the minimal basis for coordinately saturated complexes. Such exclusion is a dramatic conceptual change in the customary manner in which chemists view metal-ligand bonding. Consequently, we find that charge distribution is more ionic than conventionally supposed, energy correlation

diagrams are altered, and that interpretation of Mossbauer isomer shifts cannot be viewed in terms of 4s electron density.

We plan to extend the theory to include organometallic ligands. (A minor problem in integral evaluation appears with hydrogen, and this defect can be corrected.) The Xα theory will serve to (1) locate energies of charge transfer transitions in metalloporphyrins, (2) predict isomer shifts and quadrupole coupling constants in hemeprotein Mössbauer spectra, (3) allow discussion of the electronic formulation of HRP I, II, and (4) provide estimates of vibronic coupling constants for RR interpretation.

A major effort in writing the assembly level program for interfacing the Z-80 microcomputer with the Raman instrument is completed. Enhancement of the 874 cm^{-1} O=Os=O symmetric stretch is quite striking, being more intense than porphyrin vibrations. We plan to extend the excitation profile to the 550-620 nm and 450-350 nm region to see if the present results from 510-460 nm are followed. The current data shows a profile which follows the absorption band, a feature unlike that exhibited by porphyrin or other axial ligand modes.

In a series of OsEOP complexes: Os OEP(Co)(py), $OsEOP(OP(oMe)_3)_2$, OsOEP (NO) (OMe), and $OsEOP(O)_2$ the oxidation state marker band shifts from 1364 to 1387 cm^{-1} in the series. This shift correlates with excess electron density in the porphyrin ring, and is theonly metal besides iron which exhibits this marked change.

A series of Fe(III) OEP-phenolates have been prepared with a view to enhancing phenol vibrations. The reason for choosing this system is (1) RR spectra of Fe(III)-tyrosinate are found in several classes of metallo-enzymes, (2) the complexes model HbM, and (3) we wish to see if phenol enhancement and porphyrin enhancements share a common mechanism. This project has just started and the RR spectrum is complicated by free base fluorescence; however, repeated chromatography appears to remove the interfering fluorescence.

An excellent opportunity for observation of phenol→metal charge-transfer enhancement of phenol vibrations should occur with Mn(III)OEP(2,6-$(OMe)_2$ phenolate). We plan to synthesize the compound and search for enhancement at and to the blue of Band V, located at 444 nm. This band has exhibited enhancement of N_3^-, Cl^-,F^- vibrations in the past.

Model compounds have been synthesized with a view to preparing low-spin iron(IV), which is the state of iron in Compound II. Employing both substituted tetraphenyl porphyrin and deuteroheme as starting compounds, a series of mono-linked and bis-linked imidazole and pyridines have been prepared. We find that the binding constant of the mono-linked species is too small to provide five-coordinate iron (III), while the bis-linked species does yield the low-spin iron (III) with imidazole. However, electrolysis of the bis-linked compound yields the high-spin iron (IV) rather than the low-spin iron (IV). Also, the electrolysis product slowly (1 hour) undergoes aggregation. We think these results reflect the fact that ion-pairing is sufficiently strong to displace one (or two) imidazoles in the iron(IV) state. Additionally, we find the five-coordinate imidazole complexes are extremely sensitive to μ-oxo dimerization.

In an attempt to synthesize sterically hindered ferric prophyrins which bind OH^- but do not suffer dimerization, we have prepared the complex, tetra-(4-methyl-3,5-dipivalamidophenyl) porphyrin iron (III). This analog of Collman's "picket fence" porphyrin is a "double picket fence" but bearing substitutents at the meta rather than ortho phenyl positions. Apparently, the removal of steric constraints at the ortho position is sufficient to permit phenyl ring rotation and consequent dimerization.

It is known that one role the protein plays in oxygen activation is prevention of μ-oxo formation. No model complex yet exists which mimics this behavior. We are in the preliminary stages of preparing tetra(anthrancyl) porphyrin. The yield is small (0.5%), but we believe that the meta and ortho phenyl substitutents will prevent the phenyl ring rotation that caused the dipivalamido compound to dimerize.

All components for the nanosecond spectrometer have been bought and programming a second microcomputer for interfacing with the transient digitizer is almost complete. We should initiate the study of transients in charge-exchanging porphyrin moieties early in 1981.

The undersigned agrees to accept responsibility for the scientific and technical conduct of the project and for provision of required progress reports if a grant is awarded as the result of this application.

10/27/80
Date

Ronald H. Felton
R. H. Felton, Principal Investigator